

PROCESS FOR TREATING PARTICLES, AND
THEIR USE IN DISPERSIONS

TECHNICAL FIELD

- 5 In one of its aspects, the present invention relates to treating particles, particularly inorganic water-insoluble compounds. The treated particles are useful particularly, but not exclusively in the compounding of polymers, especially rubbers and plastics.

10 BACKGROUND ART

- It is known in the art to utilize sulfur-containing organosilicon compounds in a variety of filled rubber products. Such known uses include tire walls, tire treads, rubber hoses, rubber belts and numerous other rubber products. Depending on the formulation, selected properties of the filled rubber can be so modified.

- 15 Since the early 1980's, automobile manufacturers have been encouraging the production of low rolling-resistance tires. These tires have polymer treads containing a silica filler and a coupling agent. A number of sulfur-containing organosilicon compounds have been identified as useful in this latter regard. The improvements achieved include meeting fuel economy standards set in various countries with minimal or no sacrifice in wet traction and wear.

- 20 Examples of known coupling agents include those described in United States patent 4,704,414, published European patent application 0,670,347A1 and published German patent application 4435311A1.

- One suitable coupling agent is a mixture of bis[3-(triethoxy-silyl)propyl]monosulfane, bis[3-(triethoxysilyl)propyl]disulfane, bis[3-(triethoxysilyl)propyl]trisulfane and bis[3-(triethoxysilyl)propyl]tetrasulfane and higher sulfane homologues - for example, coupling agents available under the trade names Si-69 (average sulfane 3.5) and Silquest A-1589 or Si-75 (predominant sulfane 2.0). In the past, achieving a good balance between the

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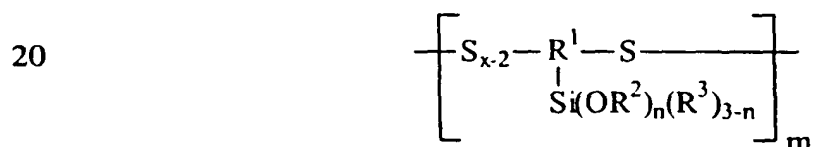
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coupling agent and particles, such as silica, without scorching or premature curing has proven difficult.

Illustrative examples of other coupling agents include the following:

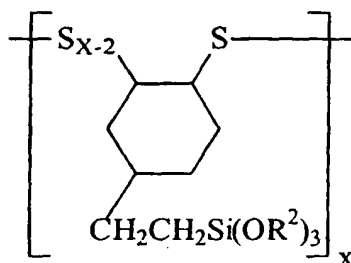
bis[2-(trimethoxysilyl)ethyl]tetrasulfane, bis[2-(triethoxysilyl)ethyl]trisulfane,
 5 bis[3-(trimethoxysilyl)propyl]disulfane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldiethoxysilane, 3-mercptoethylpropyl-ethoxymethoxysilane, 1,3-bis(3-acryloxypropyl)tetramethoxydisiloxane, acryloxypropylmethyldimethoxysilane, 3-methacryloxypropyltrimethoxysilane, allyltrimethoxysilane, diallyldiethoxysilane, 5-(bicyclo-
 10 heptenyl)triethoxysilane, 5-(bicycloheptenyl)methylmethoxyethoxysilane, isopropoxytriacyltitanate, diisopropyldimethacryltitanate, diethoxydi(3-mercaptopropoxy)zirconate, triisopropoxy-(2-mercptoethoxy)zirconate, and di[neopentyl(diallyl)oxy]-di(3-mercaptopropoxy)-zirconate.

Other known coupling agents include those disclosed in published
 15 German patent application 4435311A1 mentioned above. On pages 2 and 3 of this reference, there is disclosure of oligomers and polymers of sulphur containing organooxysilanes of the general formula:



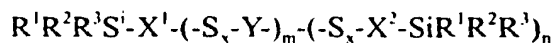
in which R¹ is a saturated or unsaturated, branched or unbranched, substituted
 25 or unsubstituted hydrocarbon group that is at least trivalent and has from 2 to 20 carbon atoms, provided that there are at least two carbon-sulphur bonds, R² and R³, independently of each other, are saturated or unsaturated, branched or unbranched, substituted or unsubstituted hydrocarbon groups with 1 to 20 carbon atoms, halogen, hydroxy or hydrogen, n is 1 to 3, m is 1 to 1000, p is 1
 30 to 5, q is 1 to 3 and x is 1 to 8.

Other coupling agents are of the general formula:



wherein R^2 , m and x have the meanings given above.

Other known coupling agents include those of the general formula:



in which R^1 , R^2 and R^3 are the same or different and are $C_{1,8}$ alkyl, $C_{1,8}$ alkoxy, phenyl or phenoxy, provided that at least one of R^1 , R^2 and R^3 is an alkoxy or phenoxy group. X^1 and X^2 are the same or different and are divalent linear or branched, optionally unsaturated $C_{1,12}$ alkyl groups, Y is a di-, tri- or tetravalent linear, branched or cyclic $C_{1,18}$ alkyl group that is optionally unsaturated and is optionally substituted by $C_{6,12}$ aryl, $C_{1,8}$ alkoxy or hydroxy groups and which can be interrupted by oxygen, sulphur or nitrogen atoms or aromatic $C_{6,12}$ aryl groups, or Y is a $C_{6,12}$ aryl or heteroaryl group, m is an integer from 1 to 20, n is an integer from 1 to 6 and x is an integer from 1 to 6.

Alternatively, it is known in the art to produce pre-treated silica material which has been produced by reacting untreated silica with a coupling agent. Such materials are available commercially under the tradenames Ciptane (PPG) and Coupsil (Degussa AG).

The prior art use of coupling agents is characterized by reacting the coupling agent with the particles of interest. In other words, the coupling agent is independently produced and thereafter reacted with the particles of interest.

While this approach has been satisfactory in the past, the expense of the coupling agent (usually obtained from an independent source) is relatively large. Thus, there is an ongoing need for an approach of treating the particles of interest to obtain the benefits of the coupling agent while minimizing the expense associated with conventional coupling agents.

More recently, there is disclosed in United States patent 5,834,536 a method to produce coated particles by means of a so-called "in-situ process" wherein the final product of the reaction of a coupling agent and particulate matter is generated without the need for the addition of the coupling agent to the particles, per se. The process is conducted in an aqueous slurry. However, so-produced particles must be removed from the slurry and dried prior to admixing further with a polymer (and ancillary ingredients such as oils, vulcanizing agents and accelerators) to make a vulcanizable compound. The admixing of the treated particles with rubber as taught in United States patent 5,834,536 is by mechanical mixing. This mixing may be accomplished on an open mill, in a mixing extruder or in an internal mixer (such as the Henschel, Welex or Banbury types) using one or more steps until the desired degree of dispersion of the treated particles is achieved.

It is well known that mechanical mixing of inorganic chemicals (such as the precipitated silica used in the rubber industry) with polymers to make vulcanizable compounds presents special difficulties in this regard because of the inherent hardness and much higher viscosity of these chemicals relative to the polymer matrix.

One general method of facilitating mixing and dispersion of these inorganic materials into polymer compounds in the factory is to use a very fine particle size inorganic material. However, this inevitably generates dust during both the material handling and mixing process and in many cases these dust particles are unacceptable from a housekeeping or worker health standpoint. Dust losses also change the ratio of the chemicals to the base polymer from what was intended in the original formulation; this may lead to poor processing or poor finished properties in the compound.

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Where possible, it would be preferable to produce masterbatches, dispersions and concentrates of these treated particles with suitable polymeric binders while the treated particles are still in a finely divided wet state.

5 DISCLOSURE OF THE INVENTION

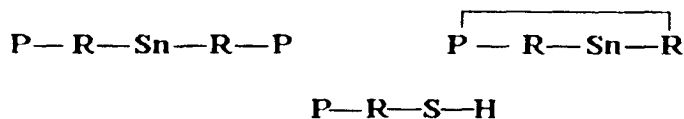
It is an object of the present invention to obviate or mitigate at least one of the above-mentioned disadvantages of the prior art.

Accordingly, in one of its aspects, the present invention provides a process for treating particles, the process comprising the step of:

10 contacting a particulate material having Formula II:



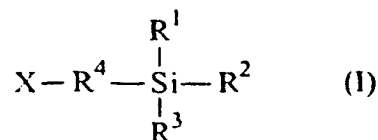
15 wherein P is a particle, R is a hydrocarbylsiloxyl moiety and X is an anion, with a sulfur-containing compound to produce a particulate material having one or more of the formulae:



wherein n is an integer from 1 to 10.

In another of its aspects, the present invention provides a process for treating particles, the process comprising the steps of:

20 (i) contacting a particulate material with a compound of Formula I:



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in which:

at least one of R^1 , R^2 and R^3 are hydroxyl or hydrolysable groups;

R⁴ is a divalent group that is resistant to hydrolysis at the Si-R⁴ bond; and
X is an anion; and

(ii) contacting the particulate material with a sulfur-containing compound.

5 Thus, the present inventor has developed a novel approach for introducing the functionality of a coupling agent into a particulate material. Specifically, the present approach does not necessitate the production of a coupling agent, per se. Rather, the approach taught herein relates to in situ production of the functional moiety of the coupling agent on the particulate
10 material (i.e., as opposed to reaction of the pre-manufactured coupling agent and the particulate material). One of the advantages of this approach is that relatively low cost chemicals can be used to produce the functional moiety of the coupling agent compared to the cost of the independently produced coupling agent, per se.

15 Preferably, the present process of treating a particulate material is carried out in an aqueous solution, suspension or slurry, so that the product of the process is an aqueous suspension or slurry of treated particles.

In one preferred embodiment, the suspension or slurry resulting from the present process, and containing the treated particles, is then mixed with a
20 hydrocarbon solution of a polymer, and then dried to form a polymer-particle dispersion. This preferred embodiment results in the production of a dispersion comprising the polymer and the treated particles. In this embodiment, the treated particles may be incorporated into a suspension without being isolated (i.e., separated from the suspension or slurry, and
25 subsequently dried). This preferred embodiment results in the production of a dispersion comprising a polymer and a treated particulate material (such as metal oxides and the like as will be discussed in more detail hereinbelow), the dispersion having been prepared from a polymer solution without the need to utilize conventional coupling agents, per se.

30 Alternatively, the treated particulate material may be separated from the suspension or slurry, and subsequently dried for later use (i.e., before addition of the polymer solution).

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In this specification, the terms "concentrate", "dispersion" and "pre-dispersion", when used in the context of the present invention, are intended to mean a composition comprising a particulate material (i.e., the additive(s) to be used for compounding purposes) and a binder therefor, wherein the

5 particulate material is the major component of the composition - i.e., the composition comprises at least about 50 percent by weight particulate material. Preferably, the composition comprises from about 50 to about 95, more preferably from about 60 to about 95, even more preferably from about 70 to about 95, percent by weight particulate material. In this specification,

10 the term "masterbatch", when used in the context of the present invention, is intended to mean a composition comprising a particulate material (i.e., the additive(s) to be used for compounding purposes) and a binder therefor, wherein the particulate material is the minor component of the composition - i.e., the composition comprises less than about 50 percent by weight

15 particulate material. Preferably, the composition comprises from about 5 to about 50, more preferably from about 20 to about 45, even more preferably from about 30 to about 40, percent by weight particulate material.

BRIEF DESCRIPTION OF THE DRAWINGS

20 Embodiments of the present invention will be described with reference to the accompanying drawing, in which:

Figure 1 illustrates an example of the use of a conventional coupling agent; and

25 Figure 2 illustrates an example of an embodiment of the present process.

BEST MODE FOR CARRYING OUT THE INVENTION

With reference to Figure 1, there is illustrated the use of a conventional coupling agent. The coupling agent illustrated is a mixture of bis[3-(triethoxysilyl)propyl]monosulfane, bis[3-(triethoxysilyl)propyl]disulfane, bis[3-(triethoxysilyl)propyl]trisulfane and bis[3-(triethoxysilyl)propyl]tetrasulfane and higher sulfane homologues, the mixture having an average sulfane content

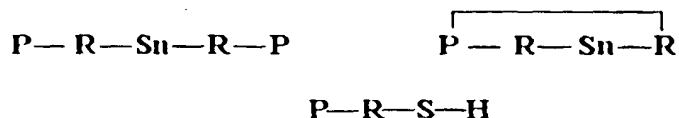
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of about 3.5 (i.e., in Figure 1, the average value for n is 3.5). Such a coupling agent is available under the trade names Si69 (Degussa AG) or Silquest®A-1289 (CKWitco). Thus, as illustrated, the alkoxy groups on one end of the coupling agent react with the pendant hydroxyl groups on a first particle to form a series of siloxyl linkages to the first particle. Further, the alkoxy groups on the other end of the coupling agent react with the pendant hydroxyl groups on a particle to form a series of siloxyl linkages to the second particle. In this fashion, the first and second particles are thus coupled to one another. Of course, it is possible for opposed ends of the coupling agent to form siloxyl linkages with the same silica particle, and indeed this is usually the case with particles that are aggregates; i.e. those particles that are much larger than molecular dimensions.

In one of its embodiments, the present process comprises the step of: contacting a particulate material having Formula II:



wherein P is a particle, R is a hydrocarbylsiloxyl moiety and X is an anion (see Figure 2 for further detail on P, R and X), with a sulfur-containing compound to produce a particulate material having one or more of the formulae:



wherein n is an integer from 1 to 10, preferably from 2 to 5.

Throughout this specification, reference is made to silica as the particle having surface hydroxyl groups since this is the preferred particulate material, but it should be appreciated that the invention applies to the use of other such minerals, and the description understood accordingly. For example, carbon

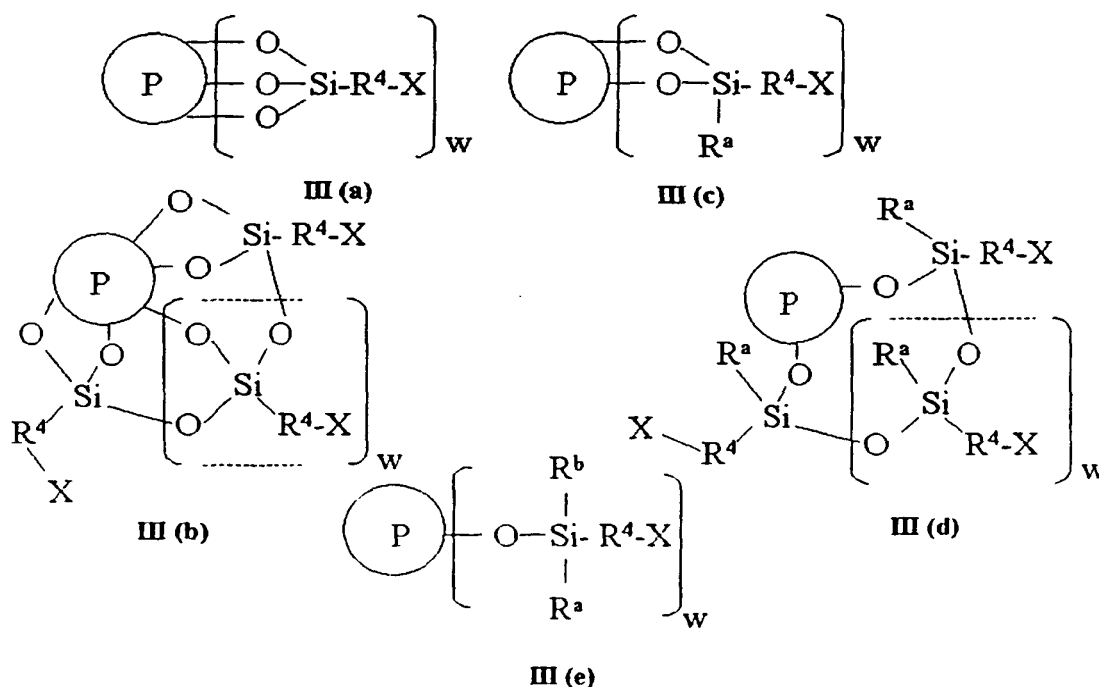
black may also be used. Further carbon-silica dual phase fillers may also be used (e.g., Ecoblack® CRX-2000).

Thus, the present invention is particularly useful to the treatment of inorganic water-insoluble compounds. Preferably the inorganic water insoluble compounds useful for treatment are those such compounds in which the chemical formula contains an oxygen atom, more preferably such compounds which the formula also contains a metal atom. More than one metal atom may be present in the chemical formula. Examples of suitable groups of useful oxygen atom compounds may be selected from the group comprising oxides, hydroxides, borates, sulfates, carbonates, silicates, phosphates, chromates and the like. Non-limiting examples of suitable oxygen atom and metal atom containing compounds may be selected from the group comprising silicon dioxide (silica), titanium oxide (titania, both rutile and anatase forms), ferric oxide, hydrated ferric oxide, ferrous oxide, antimony oxide, barium carbonate, zinc oxide, zinc borate, lead oxide (including red lead oxide), dibasic lead phosphite, lead silicate, tribasic lead sulfate and mixtures thereof. Other suitable metal atom- and oxygen atom- containing compounds, especially those which are water insoluble or only slightly soluble in water, will be readily apparent to those of skill in the art based on the foregoing discussion. For example, a particularly preferred application of the present invention is to render hydrophobic colorant or pigment particles which are typically used in the plastics industry. Non-limiting examples of suitable such particles may be selected from the group consisting of α -FeOOH (goethite), γ -FeOOH (lepidocrocite), α -Fe₂O₃ (hematite), γ -Fe₂O₃ (maghemite) and Fe₃O₄.

As stated above, the preferred particulate material for use herein is silica.

Preferably, the particles of Formula II are selected from the group comprising:

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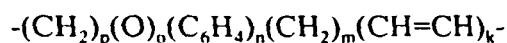
wherein:

R⁴ is a divalent group that is resistant to hydrolysis at the Si-R⁴ bond;

- 5 R^a and R^b are the same or different and each is selected from the group comprising hydroxyl, a hydrolysable group, C₁₋₄₀ alkyl, C₂₋₄₀ mono- or C₃₋₄₀ diunsaturated alkenyl and C₆₋₄₀ aromatic;

w is an integer in range of 1 to 10⁶ or more. As will be appreciated by those of skill in the art the value of w depends, at least in part, on the size of the particle and the number of pendent reactive moieties.

- 10 Preferably, R⁴ has the formula:



wherein the order of the moieties is not restricted and

- 15 k is 0 or 1,
m is a whole number in the range 0 to 20,
n is 0, 1 or 2.

o is 0 or 1, and

p is a whole number in the range 0 to 20,

with the provisos that: (i) the sum of the values of k, m, n, o and p is at least 1 and not more than 20, and (ii) if o is 1, p is 1 or greater and the sum of k, m and n is 1 or greater. More preferably, n, o and p are all 0. Most preferably, each of n, o, p and k are 0, and m is 3, i.e., R^4 is $-\text{CH}_2\text{CH}_2\text{CH}_2-$.

Preferably, in the particles of Formula II, X is selected from the group comprising acetate, chloride, bromide, iodide and sulphate, more preferably from the group comprising chloride and bromide.

The present process involves the use of a sulfur-containing compound. As used throughout this specification, the term "sulfur-containing compound" is intended to encompass any compound capable of reaction with the particles of Formula II to leave the sulfane residue in the particulate material having the Formula III, wherein n is an integer of from 1 to 10. Preferably, the sulfur-containing compound has the formula $\text{M}_{2,y}\text{S}_n$ or $\text{M}(\text{SH})_y$, where M is ammonium or a metal, y is an integer which specifies the valency of M and n is an integer of from 1 to 10.

Generally, it is preferred that the sulfur-containing compound is selected from the group comprising polysulfides, hydrosulfides and mixtures thereof. More preferably, the polysulfides comprise ammonium polysulfide compounds and alkali metal polysulfide compounds. Non-limiting examples of suitable alkali metal polysulfides may be selected from the group comprising Na_2S_n , K_2S_n and mixtures thereof, wherein n is as defined above. The most preferred sulfur-containing compound for use in the present process is Na_2S_n wherein n is as defined above. It will be clearly apparent to those of skill in the art that mixtures of the same type of sulfur-containing compound may be used. Thus, for example, when Na_2S_n is used as the sulfur-containing compound, a mixture comprising two or more of Na_2S , Na_2S_2 , Na_2S_3 , Na_2S_4 , etc. may be used to provide a desired overall average sulfane content - e.g., in the range of 2-5.

Other non-limiting examples of suitable sulfur-containing compounds include ammonium hydrosulfide (NH_4SH) and alkali metal hydrosulfide

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compounds $(M(SH)_y)$. Non-limiting examples of suitable alkali metal hydrosulfide compounds may be selected from the group comprising NaSH, KSH and mixtures thereof. The use of these hydrogen sulfide compounds will result in production of a treated particulate material having the general formula

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It is preferred to utilize the sulfur-containing compound in the form of an aqueous solution thereof. Preferably, the sulfur-containing compound is present in a concentration in range of from about 20% to about 50%, more preferably from about 25% to about 40%, most preferably from about 30% to about 40%, by weight of the aqueous solvent. Organic solvents for the sulfur-containing compounds may be used although these are less preferred.

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In a preferred embodiment, the treatment is carried out in an aqueous dispersion or slurry of the particles. Generally, the precise make up of the slurry is not particularly restricted provided that it is a mobile suspension and remains so during the treatment. Practically, it is preferred that the slurry contain up to about 60% by weight, more preferably up to about 50% by weight, of particles to be treated. While the physical nature of the particles to be treated is not particularly restricted, it is preferred that they have an average particle size in the range of from about 0.1 μm to about 100 μm , preferably from about 0.1 μm to about 50 μm , most preferably from about 1 μm to about 25 μm .

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In the preferred embodiment, the treatment is carried out in an aqueous dispersion or slurry and the concentration of the aqueous dispersion or slurry of silica particles may be between 1 and 30 percent by weight of silica in water, preferably between 5 and 25 percent by weight of silica in water and most preferably between 8 and 22 percent by weight of silica in water. Dried amorphous silica suitable for use in accordance with the invention may have a mean agglomerate particle size between 0.1 and 100 microns, preferably between 0.1 and 50 microns and most preferably between 1 and 25 microns. It is preferred that less than 10 percent by volume of the agglomerate particles

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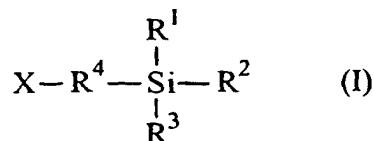
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are below 5 microns or over 50 microns in size. A suitable amorphous dried silica moreover has a BET surface area, measured in accordance with DIN (Deutsche Industrie Norm) 66131, of between 50 and 450 square meters per gram and a DBP absorption, as measured in accordance with DIN 53601, of between 150 and 400 grams per 100 grams of silica, and a drying loss, as measured according to DIN ISO 787/II, of from 0 to 10 percent by weight. If filter cake is used, it may be made by any known means such as described in Ullmann's Encyclopedia of Industrial Chemical Vol A23 pages 642-643, VCH Publishers, ©1993. The filter cake has a preferred solids content of between 5 and 30 percent by weight, most preferably between 15 and 25 percent by weight, and it may be redispersed in water in accordance with the present process to give a silica concentration of between 5 and 20 percent by weight and most preferably between 8 and 12 percent by weight. It is preferred to use a filter cake.

If a never-filtered slurry prepared from the known reaction of a solution of alkali metal silicate with either mineral acid or carbon dioxide is used, it is preferred that the solids content of the never-filtered slurry be between 1 and 30, more preferably between 5 and 10, percent by weight of silica. The slurry temperature may be between 0° and 100°C if the process is conducted at atmospheric pressure or between 0° and 135°C if the operation is conducted in a pressure vessel. Most preferably, the process is conducted at atmospheric pressure in which case the preferred temperature is between 30° and 95°C and most preferably between 45° and 90°C. The selection of atmospheric pressure or a pressure vessel is within the purview of a person skilled in the art having regard to a number of factors, including temperature and the respective volatilities of the specific reactants chosen for the process. The reaction between the particles of Formula II and the sulfur-containing compound is conducted for a period sufficient to achieve a chemical reaction between the two reactants. Generally, the time needed will depend on factors such as the reaction temperature, the parameter X in Formula II and the like, all of which are readily determined and controllable by those of skill in the art.

In a preferred embodiment of the present process, the particles of Formula II are prepared by a process comprising the step of:
contacting a particulate material with a compound of Formula I:

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10 in which:

at least one of R^1 , R^2 and R^3 are hydroxyl or hydrolysable groups; and
 X and R^4 are as defined above.

It is desirable that, prior to the addition to the silica particles of the compound of Formula I, the dispersion or slurry shall have a pH in the range
15 from 6 to about 8, more preferably from about 6.8 to about 7.2. If necessary, the pH can be adjusted by addition of acid or alkali, for example mineral acid, alkali metal hydroxide, alkaline earth hydroxide, ammonium hydroxide and the like. These can be added as such or in aqueous solution.

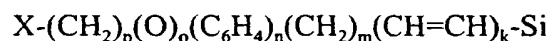
In the compound of Formula I, it is preferred that at least two, most
20 preferably all three, of the groups R^1 , R^2 and R^3 are readily hydrolysable. Suitable groups R^1 include hydroxyl groups and hydrolysable groups of formula $\text{OC}_p\text{H}_{2p+1}$, where p has a value from 1 to 10. The alkyl chain can be interrupted by oxygen atoms, to give groups, for example, of formula
25 $\text{CH}_3\text{OCH}_2\text{O}-$, $\text{CH}_3\text{OCH}_2\text{OCH}_2\text{O}-$, $\text{CH}_3(\text{OCH}_2)_4\text{O}-$, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}-$,
 $\text{C}_2\text{H}_5\text{OCH}_2\text{O}-$, $\text{C}_2\text{H}_5\text{OCH}_2\text{OCH}_2\text{O}-$, or $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{O}-$. Other suitable hydrolysable groups include phenoxy, acetoxy, chloro, bromo, iodo, ONa, OLi, OK or amino or mono- or dialkylamino, wherein the alkyl group(s) have 1 to 30 carbon atoms.

R^2 and R^3 can take the same values as R^1 , provided that only one of R^1 ,
30 R^2 and R^3 is chloro, bromo or iodo. Preferably, only one or two of R^1 , R^2 and R^3 is hydroxyl or ONa, OLi or OK.

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Non-limiting examples of groups R^2 and R^3 that are not hydrolysable include C_{1-40} alkyl, C_{2-40} mono- or C_{3-40} diunsaturated alkenyl and C_{6-40} aromatic, preferably C_{1-10} alkyl, C_{2-10} mono- or diunsaturated alkenyl and phenyl. It is preferred that R^1 , R^2 and R^3 are all the same and are CH_3O- , C_2H_5O- or C_3H_8O- . Most preferably they are all CH_3O- .

The divalent group R^4 is preferably such that $X-R^4-Si$ is of the formula:



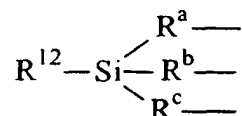
- 10 in which k , m , n , o and p are all whole numbers. The order of the moieties between X and Si is not particularly restricted other than neither X or O should be directly bound to Si , nor should there exist the bond $X-O$. The value of k is 0 or 1, the value of m is from 0 to 20 inclusive, the value of n is 0, 1 or 2, the value of o is 0 or 1 and the value of p is from 0 to 20 inclusive, with the
- 15 provisos that the sum of the values of k , m , n , o and p is at least 1 and not more than 20 and that if o is 1, m is 1 or greater or the sum of k , m and n is 1 or greater, i.e. that the Si atom is linked directly to a carbon atom. There should be no hydrolysable bond between the Si and X atoms. Preferably, m is 3 and 1, n , o and p are all 0, i.e., R^4 is $-CH_2CH_2CH_2-$.
- 20 Without wishing to be bound by any particular theory or mode of action, it is believed that the mechanism of the present process can be illustrated with reference to Figure 2. In the embodiment illustrated in Figure 2, the particulate material being treated is silica, R^1 , R^2 and R^3 are each $-OCH_3$, R^4 is $-CH_2CH_2CH_2-$, X is $-Cl$ and the sulfur-containing compound is Na_2S_n .
- 25 Thus, in the illustrated embodiment, 3-chloropropyltrimethoxysilane is reacted with the untreated silica particle to produce the illustrated treated particle having a chloropropylsiloxyl moiety (this an example of the particle of Formula II). In the second step, two such treated particles are reacted with Na_2S_n to produce the illustrated coupled particulate material. Thus, as will be
- 30 apparent to those of skill in the art, while the product of the process in Figure 2 is the same as that in the process of Figure 1, the coupling agent, *per se*, was not produced in the former. Also, as will be appreciated by those of skill in

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the art, in the second step, it is possible for the sulfur-containing compound, Na_2S_n , to react with a single silica particle.

In a preferred embodiment the particles have also bonded thereto an aminohydrocarbonsilane moiety having the formula:

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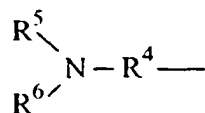
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in which:

R^a , R^b and R^c are the same or different and each is selected from -O- and $-\text{C}_p\text{H}_{2p}-$, optionally substituted by one or more oxygen atoms and wherein p is an integer of from 1 to 10; and

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R^{12} is a group of formula:



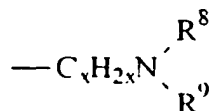
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or an acid addition or quaternary ammonium salt thereof in which:

R^4 is a divalent group that is resistant to hydrolysis at the $\text{Si}-\text{R}^4$ bond;

R^5 is selected from: hydrogen; a C_{1-40} alkyl; a C_{2-40} mono-, di- or tri-unsaturated alkenyl group; a C_6-C_{40} aryl group; a group of the formula:

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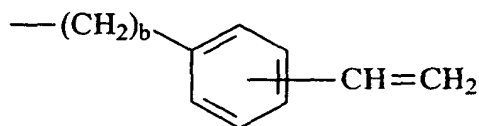
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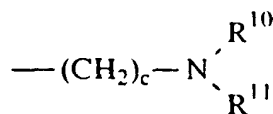
-17-

in which x is an integer from 2 to 10, R^8 and R^9 , which may be the same or different, are each selected from: hydrogen; C_{1-18} alkyl; C_{2-18} mono-, di- or tri-unsaturated alkenyl; phenyl; a group of formula:

5



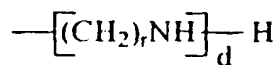
10 wherein b is an integer from 1 to 10; a group of formula:



15

wherein c is an integer from 1 to 10, and R^{10} and R^{11} may be the same or different and are each selected from: hydrogen, C_{1-10} alkyl group or C_{2-10} alkenyl group, provided that there is no double bond in the position alpha to the nitrogen atom; and a group of formula:

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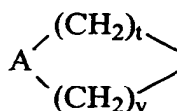
wherein r is an integer from 1 to 6 and d is an integer from 1 to 4;

R^6 may be any of the groups defined for R^5 with the provisos that: (i) R^5 and R^6 do not have a tertiary carbon atom adjacent to the nitrogen atom, and (ii) at least one of R^5 and R^6 has a carbon chain at least 8 carbon atoms in length uninterrupted by any heteroatoms;

30

or R^5 and R^6 may together form a divalent group of formula:

-18-



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in which A is selected from: a -CHR group or a -NR group in which R is hydrogen or a C₆₋₄₀ alkyl or C₆₋₄₀ alkenyl group, a C₆-C₄₀ aryl group, an oxygen atom and a sulfur atom, and t and v are each independently 1, 2, 3 or 4;

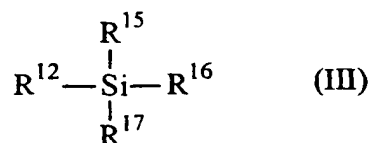
10 provided that the sum of t and v does not exceed 6, preferably the sum of t and v is 4.

In published International patent applications WO 98/52954 [Koski #1] and WO 98/53004 [Koski #2], there is taught a novel approach for producing masterbatches of polymers and particles. Generally, this approach, as taught in Koski #2, relates to initially rendering the particles hydrophobic to facilitate dispersion thereof in the polymer. Hydrophobicity is conferred to the particles by reacting the particles with a particular aminohydrocarbon silane compound to form the above aminohydrocarbonsilane moiety on the surface of the particles. A particularly preferred process to produce a useful aminohydrocarbon silane compound and a subset of aminohydrocarbon silane compounds are taught in Koski #1. Alternatively, the above aminohydrocarbonsilane moiety can be formed on the surface of the particles in situ using the approach described in copending Canadian patent application 2,254,315 (Bayer Ref: POS-1061), filed on November 20, 1998. If the particle has an aminohydrocarbonsilane moiety formed thereon, it is preferred that the amount of sulfur-containing compound used in the present process is less than the stoichiometric amount necessary to react with substantially all of the pendant reactive groups on the surface of the particles.

In a preferred embodiment of the present process, the product of the present process is further reacted with a compound of Formula III:

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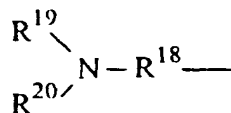
in which:

R^{15} , R^{16} and R^{17} have the same definitions as R^1 , R^2 and R^3 in Formula

10 I hereinabove; and

R^{12} is selected from the group comprising a C_{8-40} alkyl group or a C_{8-40} mono-, di- or tri-unsaturated alkenyl group, either of which can be interrupted by one or more aryl groups, preferably phenyl groups; a group of formula:

15



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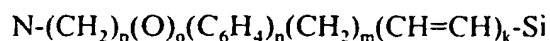
or an acid addition or quaternary ammonium salt thereof in which R^{18} is a divalent group resistant to hydrolysis at the Si- R^{18} bond, R^{19} is selected from the group comprising hydrogen, a C_{1-40} alkyl group, a C_{2-40} mono-, C_{3-40} di- or C_{4-40} tri-unsaturated alkenyl group, a substituted aromatic group, for example the phenylene group $-(\text{C}_6\text{H}_4)-$, the biphenylene Group $-(\text{C}_6\text{H}_4)-(\text{C}_6\text{H}_4)-$, the $-(\text{C}_6\text{H}_4)-\text{O}-(\text{C}_6\text{H}_4)-$ group or the naphthylene group, $-(\text{C}_{10}\text{H}_6)-$, the aromatic group being unsubstituted or substituted by a C_{1-20} alkyl or C_{2-20} mono-, di- or tri-unsaturated alkenyl group; and R^{20} may be any of the groups defined for R^{19} , with the provisos that R^{19} and R^{20} do not have a tertiary carbon atom adjacent to the nitrogen atom and that at least one of R^{19} and R^{20} has a carbon chain at least 8 carbon atoms in length uninterrupted by any heteroatoms.

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-20-

Preferably, R^{18} is a C_1 - C_{40} saturated or unsaturated group (e.g., alkenyl, aryl, cycloalkyl and the like).

In this preferred embodiment, again, it is preferred that the particulate filler material, more preferably a mineral filler, is in the form of an aqueous slurry or a dispersion, and the compound of Formula III is added to the slurry or dispersion under intense mixing. In the compound of Formula III the possible and preferred values for R^{15} , R^{16} and R^{17} are the same as the possible and preferred values for R^1 , R^2 and R^3 that are discussed above in relation to Formula I. If R^{12} is an amino group of formula $-R^{18}-NR^{19}R^{20}$, preferred values for R^{18} are such that $N-R^{18}-Si$ includes groups of the formula:



in which k is 0 or 1, m is 0 to 20 inclusive, n is 0, 1 or 2, o is 0 or 1 and p is 0 to 20 inclusive, provided that the sum of k , m , n , o and p is at least 1 and not greater than 20, and further provided that if o is 1, p is also 1 or greater, and the sum of k , m and n is 1 or greater. The order of the moieties between N and Si is not particularly restricted other than neither N or O should be directly bound to Si and there should be no $N-O$ bond. There should be no hydrolysable group between the silicon and nitrogen atoms. Preferably k , n , o and p are all 0 and m is 3, i.e. R^{18} is $-CH_2CH_2CH_2-$.

R^{12} may be a moiety containing at least one primary, secondary, or tertiary amine nitrogen. In this case the amino group bonded to R^{18} is given by the formula $-NR^{19}R^{20}$. R^{19} may be a H or a C_{1-40} alkyl group or a C_{2-40} mono-, di- or tri-unsaturated alkenyl group. R^{19} may also be a C_{1-20} alkyl-substituted or C_{2-20} alkenyl-substituted aromatic group. The aromatic group may be, for example, the phenylene group $-(C_6H_4)-$, the biphenylene group $-(C_6H_4)-(C_6H_4)-$, the $-(C_6H_4)-O-(C_6H_4)-$ group, or the naphthylene group $-(C_{10}H_6)-$. R^{20} may be one of the same groups as R^{19} with the further proviso that at least one of R^{19} and R^{20} must contain a continuous carbon chain of at least 8 carbons in length, uninterrupted by any heteroatoms.

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As stated above, if R^{19} and R^{20} are other than hydrogen, the carbon atom attached to the nitrogen atom is not tertiary. Preferably the carbon atom attached to the nitrogen atom is primary, i.e., $-CH_2-$.

It is preferred that R^{19} is a mono-unsaturated alkenyl group of 12-20
5 carbons in length and most preferable that R^{19} is a monounsaturated alkenyl group of 16 to 18 carbons in length. It is most preferable also that R^{20} is H. Alternatively, R^{12} may be a moiety which contains a mineral acid salt or a quaternary ammonium salt of an amine. The formula of R^{12} may thus be described by the extended formula $-R^{18}-NR^{19}R^{20}R^{21}X$ wherein $-R^{18}-$, R^{19} and
10 R^{20} are as previously defined and R^{21} may be a H, or a C_{1-40} alkyl or C_{2-40} mono-, di- or tri-unsaturated alkenyl group and X is an anion, preferably Cl or Br, although sulphate can be used.

If the compound of Formula III is used, there is the further proviso that at least one of R^{19} and R^{20} must contain a continuous carbon chain of at least 8
15 carbons in length, uninterrupted by any heteroatom. It is preferred to use an amine salt where R^{19} is a mono- or di-unsaturated alkenyl group of 12-20 carbons in length and most preferably that R^{19} is a mono- or di-unsaturated alkenyl group of 16 to 18 carbons in length. It is most preferable also that R^{20} is H and that R^{21} is H and X is chlorine. The preferred hydrophobicizing agent
20 of Formula III is N-oleyl-N-(3-trimethoxysilyl)propyl ammonium chloride.

Preferably, the amount of the hydrophobic compound of Formula III to add is generally between 0.5 and 20 percent by weight of the weight of the particles (preferably mineral particles such as silica) in the slurry (dry basis), and is inversely proportional to the particle size of the silica particles. The
25 compound may be added to the slurry in its natural state, either as a liquid or a solid. However, to facilitate dispersion, it is preferred, where possible, to add the compound as a liquid. If the melting point of the compound is below $95^{\circ}C$, it is preferred to add it to the slurry in a molten state at a temperature at least $5^{\circ}C$ above the melting point, provided the temperature of the compound
30 in the liquified state does not exceed $100^{\circ}C$ and provided that the compound does not decompose under these conditions. If the melting point exceeds $95^{\circ}C$, it is most preferred to use a solvent. Suitable solvents are alcohols

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containing 1 to 5 carbon atoms and most preferably those containing 1 to 3 carbon atoms, that is to say methanol, ethanol, n-propanol or isopropanol. If the compound of Formula III is an alkoxysilane, most preferably the alkoxy group of the solvent alcohol will be the same as the alkoxy group of the alkoxysilane. For example, if the compound of Formula III is a methoxysilane, the preferred solvent is methanol. The concentration of the compound in the solvent may be from 10 to 90 percent by weight and most preferably between 25 and 75 percent by weight and most preferably 50 percent by weight. Preferably, the solution is prepared and added to the slurry at a temperature between a lower limit of 0°C and an upper limit which is the lower of at least 10°C below the boiling point of the solvent and 95°C.

After the addition of the hydrophobic compound of Formula III which is added, the equivalent balance (EB) should be calculated to determine how much, if any, mineral acid or alkali metal hydroxide (or solutions thereof) to add. The equivalent balance (EB) may be determined from the absolute value of the sum of the group values of X, R¹⁵, R¹⁶ and R¹⁷ and the weight added, and the molecular weight of the compound, according to the following scheme: The group contribution of X for either X=Cl or X=Br is -1, thus if X is present it is given a value of -1. The group contribution of each of R¹⁵, R¹⁶ and R¹⁷ is generally zero for all groups except as follows: if the group is CH₃COO[⊖], Cl[⊖] or Br[⊖], in which case it is -1, or if it is amino, ONa, OK, or OLi in which case it is +1. If the sum of the group contributions for X, R¹⁵, R¹⁶ and R¹⁷ is zero, no adjustment with mineral acid or alkali metal hydroxide (or solutions thereof) is necessary. If the sum of the group values is a positive integer, adjustment with mineral acid is desirable, and if it is negative, adjustment with alkali hydroxide is desirable.

For example, where R¹⁵=OC₂H₅, R¹⁶=OCH₃, R¹⁷=CH₃ and X=Cl, the sum \sum of the group values (g.v.) is:

$$\sum = (\text{g.v. OC}_2\text{H}_5) + (\text{g.v. OCH}_3) + (\text{g.v. CH}_3) + (\text{g.v. Cl}) = (0) + (0) + (0) + (-1) = -1.$$

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The negative sign in front of the sum indicates adjustment with alkali metal hydroxide is required. The number of equivalents of alkali required is given by the equivalent balance (EB) which includes the absolute value of the sum of the group contributions ($|\sum|$) as a scaling factor.

5

$$EB = \frac{|\sum| \times \text{weight in grams of the compound added}}{\text{molecular weight of the added chemical.}}$$

In continuing the example, if a process according to the present invention were scaled so as to require 3450 grams of a compound of Formula III with a molecular weight of 466 grams and the sum of the group values gave -1, EB would be calculated as follows:

15

$$EB = |-1| \times 3450/466 = 7.4 \text{ gram-equivalents.}$$

Thus, in this example, 7.4 gram-equivalents of alkali metal hydroxide would be added. Sodium hydroxide is the preferred alkali metal hydroxide. The weight of sodium hydroxide added would be:

$$\text{Weight} = (EB) \times (\text{Equivalent Weight of NaOH}) = 7.4 \times 40.0 = 296 \text{ grams.}$$

The preferred technique according to the invention is to dissolve the alkali hydroxide or mineral acid in water so as to obtain a concentration between 5 and 25% by weight and most preferably between 5 and 10% by weight prior to adding the solution to the slurry. The temperature of the solution may be from 0° to 100°C under atmospheric pressure, or if a pressure vessel is used for preparation of the solution, it may be from 0° to 130°C. It is preferred that the temperature of the solution be within 10°C of the solution of the slurry. The dispersion of the solution in the slurry is effected by mixing. The product of this preferred embodiment of the present process described thus far relates an aqueous slurry or dispersion of hydrophobicized particles

(i.e., it has not yet been contacted with a polymer or other substrate to be filled), which can be used as such or can be filtered and dried.

The hydrophobicized particles may be used as a compounding agent in a multitude of materials including, but not limited to, the following: polymers,
5 alkyd paints, toners such as those used in photocopiers, modified plastics and rubber vulcanizates.

In a preferred embodiment of this invention the hydrophobicized particles, in the aqueous dispersion or slurry, is incorporated into a polymer, for example an elastomer to form a rubber masterbatch. The slurry is mixed
10 with a hydrocarbon or other solution of the elastomer. Preferably, the solvent in which the elastomer is dissolved is immiscible with, or mostly immiscible with, water to form a preblend. This elastomer solution may be made by dissolving the solid elastomer in a solvent, or it may be the solution resulting from the polymerisation of monomers in the solvent. The elastomer may be a
15 hydrocarbon rubber, a graft polymer or block polymer of monomers having at least one ethylenically unsaturated bond and polymerizable through this unsaturation. Other suitable polymers include, but are not limited to butyl rubber (IIR), halogenated butyl rubber (HIIR), cis-1,4-polyisoprene rubber (IR), ethylene-propylene-diene monomer (EPDM) rubber, ethylene-propylene
20 monomer (EPM) rubber, styrene-butadiene rubber (SBR), polybutadiene rubber (BR), acrylonitrile-butadiene rubber (NBR), hydrogenated acrylonitrile-butadiene rubber (HNBR), HSRE, natural rubber (NR), polystyrene (PS), chloroprene¹ rubber (CR), ethylene-vinyl acetate (EVM) rubber, epichlorohydrin (ECO) rubber, chlorinated polyethylene, silicone
25 rubber (Q), urethane rubber (AU EU), acrylonitrile-butadiene-styrene (ABS) polymers and the like. Suitable solvents include but are not limited to cyclohexane, hexane, benzene, toluene and pentane. Optionally, processing oil and antioxidants may be added to the hydrocarbon solution prior to mixing with the slurry, or they may be added after mixing the slurry and the elastomer
30 solution.

¹Also known as Neoprene™.

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The viscosity of the final elastomer solution, sometimes referred to as an elastomer cement, containing the optional ingredients is preferably such that it closely matches the viscosity of the silica slurry and is generally between 1,000 and 50,000 centipoise. The temperature of the elastomer solution is preferably the same as that of the slurry and the amount of cement that is added is such that the final masterbatch may contain from 5 to 250 parts of silica per hundred parts of elastomer, preferably from 35 to 100 parts of silica per hundred parts of elastomer, most preferably from 60 to 80 parts of silica per hundred parts of elastomer.

The elastomer cement and, optionally, oil and antioxidants, is mixed with the silica slurry until the mixture becomes homogeneous and the milky colour of the silica slurry disappears to form a preblend. A small amount of water may separate at this stage.

If not added previously, or if additional amounts are desired, oil and antioxidants may be added next and the mixing continued further until the oil and antioxidant become incorporated in the continuous phase.

Any water which separates from the preblend may be removed, discarded or recycled for silica slurry make-up by stopping the agitator for a suitable period and allowing the water phase to accumulate in the bottom of the mixing tank from which it may be drained prior to proceeding with the next step. Agitation is preferably restarted after the water layer is removed.

If antioxidants and processing oil were not previously added, or if additional amounts are desired, they may be added at this stage and stirring continued until the preblend is again homogeneous.

The preblend is then added to water heated to a temperature equal to, or preferably higher than the boiling point of the solvent used for the elastomer cement so as to remove the solvent and produce a masterbatch coagulum in the form of a crumb suspended in water. The preferable temperature of the water prior to addition of the preblend is between 50° and 100°C, most preferably between 90° and 95°C, and the preblend is added at a rate so as to maintain a so-fixed or reasonably so-fixed water temperature throughout the coagulation. The agitation is set sufficiently high so as to maintain the crumb in a

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suspended state within the water but not so high as to cause the crumb to subdivide into particles smaller than approximately 5 millimeters.

The solvent may be recovered from the coagulator by recondensing the vapours. The material containing the suspended crumb is passed through a filter screen sized so as to recover the wet masterbatch. The material passing through the screen may be optionally recycled for further silica slurry make-up.

The wet crumb is dried such as by using forced air or fluidized bed or microwave drying techniques at a temperature between about 75° and about 135°C, preferably between about 85° and about 120°C, most preferably between about 85° and about 105°C, until a suitably dry masterbatch crumb is obtained.

The dried crumb may be further processed according to industry and customer requirements.

Another advantageous application of the hydrophobicized particles is in the production of predispersions or concentrates of polymer compounding chemicals. These materials typical include a chemical of interest which is predispersed in high concentrations (at least about 50 percent by weight as discussed hereinabove) in a binder, preferably a polymeric material, and are supplied in the form of pellets, slabs and the like. Thus, the polymer acts as a binder for the chemical of interest. The chemical of interest may, for example, be a silica filler, a colorant, a pigment, an inorganic activator, a stabilizer and/or a flame retardant for use to produce a polymer-based product.

In a preferred embodiment of this invention the hydrophobicized particles, in the aqueous dispersion or slurry, are incorporated into a binder material, for example a polymer in the form of a polymer solution or cement. The slurry of treated particles is mixed with a hydrocarbon or other non-aqueous solution of the binder. Preferably, the solvent in which the binder is dissolved is immiscible with, or mostly immiscible with, water to form a preblend. This binder solution (e.g., polymer cement) may be made by dissolving the solid polymer in a solvent or, in the case of a solution polymer,

it may be the solution resulting from the polymerisation of monomers in the solvent.

Preferably, the binder is a polymer. It will, however, be appreciated by those of skill in the art that the binder may be a quasi- or non-polymeric material such as a polyethylene wax, a rosin, a fatty acid, a high molecular weight liquid and the like, or a combination of polymer and such quasi- or non-polymeric material.

The polymer may be an elastomer (e.g., a hydrocarbon rubber), a graft polymer or block polymer of monomers having at least one ethylenically unsaturated bond and polymerizable through this unsaturation, a plastic and the like.

Elastomers are well known to those of skill in the art. Non-limiting examples of suitable elastomers may be selected from the group comprising natural rubber (NR), depolymerized NR, cis-1,4-polyisoprene rubber (IR), polybutadiene rubber (BR), styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR), hydrogenated acrylonitrile-butadiene rubber (HNBR), butyl rubber (IIR), halogenated butyl rubber (HIIR), ethylene-propylene monomer (EPM) rubber, ethylene-propylene-diene monomer (EPDM) rubber, chloroprene rubber (CR), ethylene-vinyl acetate (EVM) rubber, silicone rubber (Q), epichlorohydrin (ECO) rubber, urethane rubber (AU EU) and the like.

Plastics are well known to those of skill in the art. Non-limiting examples of suitable plastics may be selected from the group comprising polystyrene, polyethylene, polypropylene, chlorinated polyethylene, acrylonitrile-butadiene-styrene (ABS) polymers, ethylene-vinyl-acetate (EVA) plastic, polyvinyl chloride (PVC), plasticized polyvinyl chloride (PVC), polymethylmethacrylate (PMMA), epichlorohydrin (ECO) plastic and the like. Of course those of skill in the art will recognize and appreciate that the foregoing materials may be modified with respect to parameters such as monomer sequence, monomer ratio, molecular weight (M_n , M_w , etc.), molecular weight ratio and the like while still being useful in the present invention.

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The selection of a suitable solvent for preparation of the polymer binder solution is within the purview of a person skilled in the art and depends on the specific polymer to be dissolved. Non-limiting examples of suitable solvents may be selected from the group comprising cyclohexane,

5 chlorobenzene, hexane, benzene, toluene, pentane and the like. Optionally, processing oil, antioxidants and other chemicals known in the art as processing aids may be added to the hydrocarbon solution prior to mixing with the slurry, or they may be added after mixing the slurry and the polymer solution.

10 The viscosity of the final polymer solution, sometimes referred to as a polymer cement, containing the optional ingredients, is preferably such that it closely matches the viscosity of the slurry of treated particles and is generally between 1,000 and 50,000 centipoise. This may depend, at least in part on the specific gravity and/or particle size of the particles dispersed in the slurry. The temperature of the polymer solution is preferably the same as that of the

15 slurry. Further, it is preferred to add the polymer cement in an amount such that the final dried dispersion may contain the treated particulate material as the major component of the composition - i.e., the dispersion comprises at least about 50 percent by weight particulate material. Preferably, the dispersion comprises from about 50 to about 95, more preferably from about

20 60 to about 95, even more preferably from about 70 to about 95, percent by weight particulate material.

The polymer cement and, optionally, oil and antioxidants, is mixed with the slurry of treated particles until the mixture becomes homogeneous. This is confirmed by assessing the uniformity of colour and/or solids

25 dissolution (i.e., the present of a substantially single phase, although a small insubstantial amount of water may separate at this stage).

If not added previously, or if additional amounts are desired, oil and antioxidants may be added next and the mixing continued further until the oil and antioxidant become incorporated in the continuous phase.

30 Any water which separates from the preblend may be removed, discarded or recycled for slurry make-up by stopping the agitator for a suitable period and allowing the water phase to separate in the mixing tank from which

it may be removed prior to proceeding with the next step. Agitation is preferably restarted after the water layer is removed.

5 If antioxidants and processing oil were not previously added, or if additional amounts are desired, they may be added at this stage and stirred to disperse them.

10 The preblend is then added to water heated to a temperature equal to, or preferably higher than the boiling point of the solvent used for the polymer cement so as to remove the solvent and produce a dispersion coagulum in the form of a crumb suspended in water. Preferably, the temperature of the water prior to addition of the preblend is in the range of from about 50°C to about 100°C, more preferably in the range of from about 90°C and to about 95°C. Further, it is preferred to add the preblend at a rate so as to maintain a temperature substantially within thereof preferred ranges. The agitation is set sufficiently high so as to maintain the crumb in a suspended state within the 15 water, but not so high as to cause the crumb to subdivide into particles smaller than approximately 5 mm.

20 The solvent may be recovered from the coagulator by condensing the vapours. The material containing the suspended crumb may then be passed through a filter screen sized so as to recover the wet composition. The filtrate from this step may be optionally recycled for further slurry make-up.

25 The wet crumb is dried such as by using forced air or fluidized bed or microwave or other drying techniques. If microwave or other drying techniques are used, it is preferred to conduct these at a temperature in the range of from about 75°C to about 135°C, preferably in the range of from about 85°C to about 120°C, most preferably in the range of from about 85°C to about 105°C, until a suitably dry dispersion crumb is obtained.

The dried crumb may be further processed according to industry and customer requirements.

30 Embodiments of the present invention will be illustrated with reference to the following Examples which should not be used to construe or limit the scope of the invention.

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Example 1

In this Example, the following materials were used:

Hi-Sil® 233

5

3-chloropropyltrimethoxysilane

sodium tetrasulfide solution

Buna®VSL 5025-1 (oil extended solution SBR) cement in hexane

Vulcanox® 4020

N-oleyln-N-(trimethoxysilyl) propyl ammonium chloride

10

In a 4 L glass beaker in a fumehood were combined 510 grams of Hi-Sil 233 (amorphous precipitated silica) and 2040 grams of water and the resulting mixture was stirred vigorously with an electrically driven stirrer equipped with a radial impeller until a smooth slurry was obtained. The beaker was place on a hot plate and the slurry was heated to 50°C while under high agitation. N-oleyln-N-(trimethoxysilyl) propyl ammonium chloride as 5.0 grams of a 50 wt% solution in methanol was added into the vortex over 5 minutes. A marked thickening was noted. Sodium hydroxide, 0.218 grams was dissolved in 10 mL of water and shaken to dissolve. This solution was added to the vortex over 1 minute. The sides of the beaker were then washed down with a small amount of water.

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With the slurry at 50°C, 3-Chloropropyltrimethoxysilane (30.1 gm, 152 millimoles) was added to the vortex dropwise over 5 minutes and stirring was continued for 30 minutes. The above slurry was then heated to 60°C while agitation was maintained. Sodium tetrasulfide solution (28.5 grams of 34 wt% Na_2S_4 in water) was then added over 15 minutes. The colour gradually changed from a dark yellow through greenish-grey to a Kelly green. The slurry was stirred for an additional 5 hours while the temperature was held at between 60-62°C. When the slurry became too thick for good agitation, additional water was added as required to enable circulation to be maintained. Slurry volume was maintained at around 2500 mL. After the end of the period the slurry had returned to a white colour. N-oleyln-N-(trimethoxysilyl) propyl

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ammonium chloride as 46.0 grams of a 50 wt% solution in methanol was added into the vortex in 1 mL aliquots over 5 minutes. A marked thickening was noted. Sodium hydroxide, 2.07 grams was dissolved in 25 mL of water and shaken to dissolve. This solution was added to the vortex in 1 mL aliquots over 1 minute. The sides of the beaker were then washed down with a small amount of water and the heater and stirrer were turned off.

When cool, the cement was quantitatively transferred to a 2.5 gallon plastic bucket in the fume hood by using a spatula and a small amount (~50 mL) of water from a wash bottle. Oil extended solution styrene-butadiene copolymer cement (3188 grams of 20 wt% Buna® VSL 5025-1 in cyclohexane) and Vulcanox® 4020 antioxidant (5.0 grams) were then added and the mixture was stirred manually with a spatula to homogenize.

Homogenization was continued with an air stirrer for an additional 5 minutes. The mixture became extremely viscous and elastic during this time. Small beads of water which separated were crystal clear. An additional 500 mL of cyclohexane solvent was then added in order for the air stirrer to cope with the viscosity of the mixture.

Coagulating to remove the solvent was done in a fumehood. The blend was added slowly to stirred water which was maintained at 92-95°C using low pressure steam. The aqueous coagulation serum was somewhat turbid towards the end of the coagulation and some foaming was experienced. The wet crumb was isolated by screening through a 1-mm sieve, water washed and then dried for 4 hours at 85 degrees Celsius. Product yield was 1313 grams, dry basis.

The coagulation serum was then cooled and passed through Whatman #41 filter paper in order to pick up any unincorporated silica. The filter paper was then dried at 85°C. A total of 22.3 grams of silica was recovered. The filler incorporation efficiency was calculated as 95.6%.

30 Example 2

The ingredients and conditions of Example 1 were repeated with the exception that 3188 grams of a 20 wt% solution of Buna® CB24

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polybutadiene rubber in hexane and 191 grams of Sundex® 8125 were added to the treated slurry in place of the oil extended solution styrene-butadiene copolymer cement. Product yield was 1306 grams, dry basis.

5 The coagulation serum was then cooled and passed through Whatman #41 filter paper in order to pick up any unincorporated silica. The filter paper was then dried at 85°C. A total of 6.1 grams of silica was recovered. The filler incorporation efficiency was calculated as 98.8%.

10 While the present invention has been described with reference to preferred embodiments and illustrative Examples, it will of course be understood by those of skill in the art that various modifications to these preferred embodiment and illustrative Examples may be made without departing from the spirit and scope of the invention.

15 All publications, patents and patent applications referred to herein are incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety.

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